SUPPORTING INFORMATION

AFM-IR and IR-SNOM for the Characterization of Small Molecule Organic Semiconductors

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Optical micrographs of single crystals

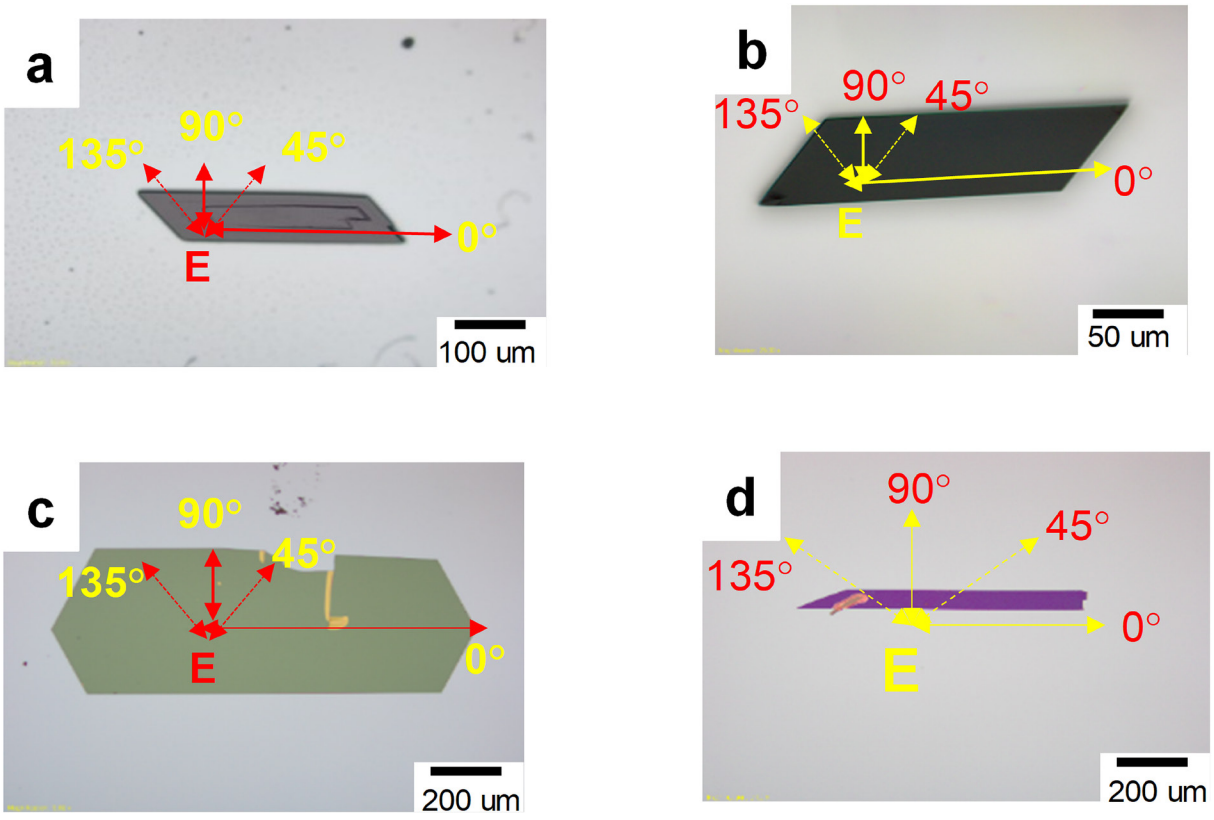

Figure S1. Optical micrographs of single crystals of (a) TIPS-PEN, (b) TIPS-TAP grown by the drop-casting method, (c) Rubrene and (d) PDIF-CN_2, grown via physical vapor transport method. Also indicated are the angles that correspond to the orientation of the in-plane electric field with respect to the long axis of the crystal.

Calculated IR spectra

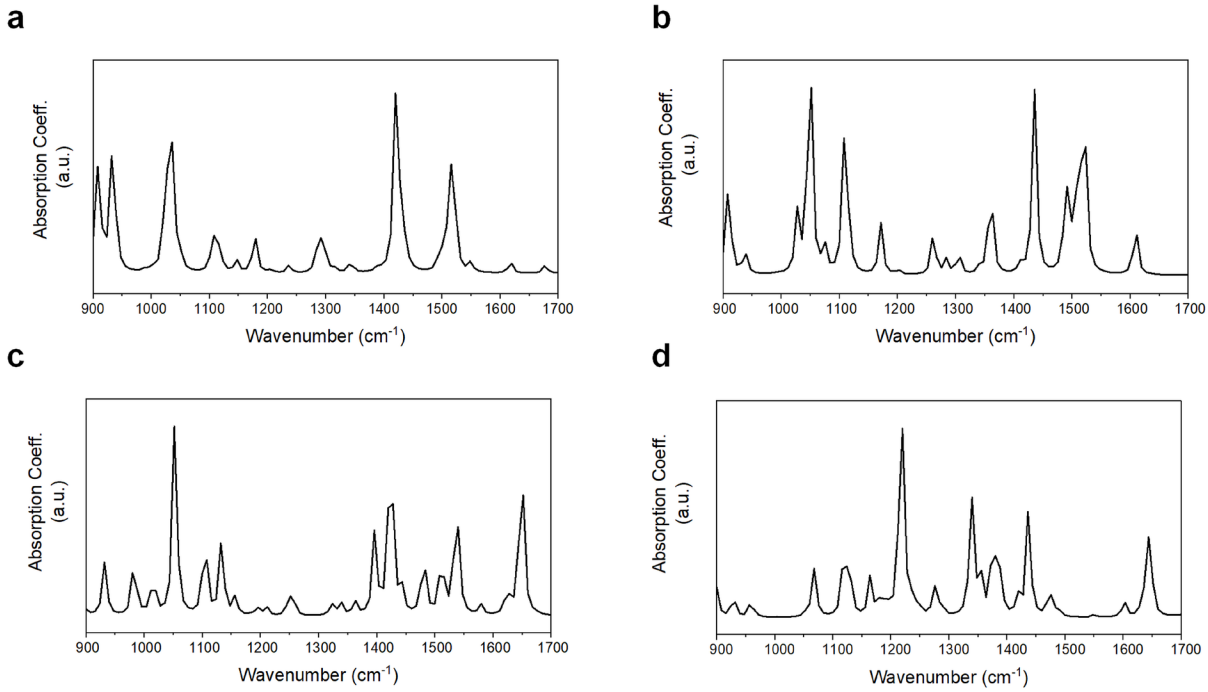

Figure S2. Calculated IR spectra of (a) TIPS-PEN, (b) TIPS-TAP, (c) Rubrene and (d) PDIF-CN_2. All spectra were broadened using Lorentzian functions with a full-width at half maximum of 4 cm^{-1}. No energy scaling or frequency correction was applied.

IR-SNOM near-field amplitude spectra

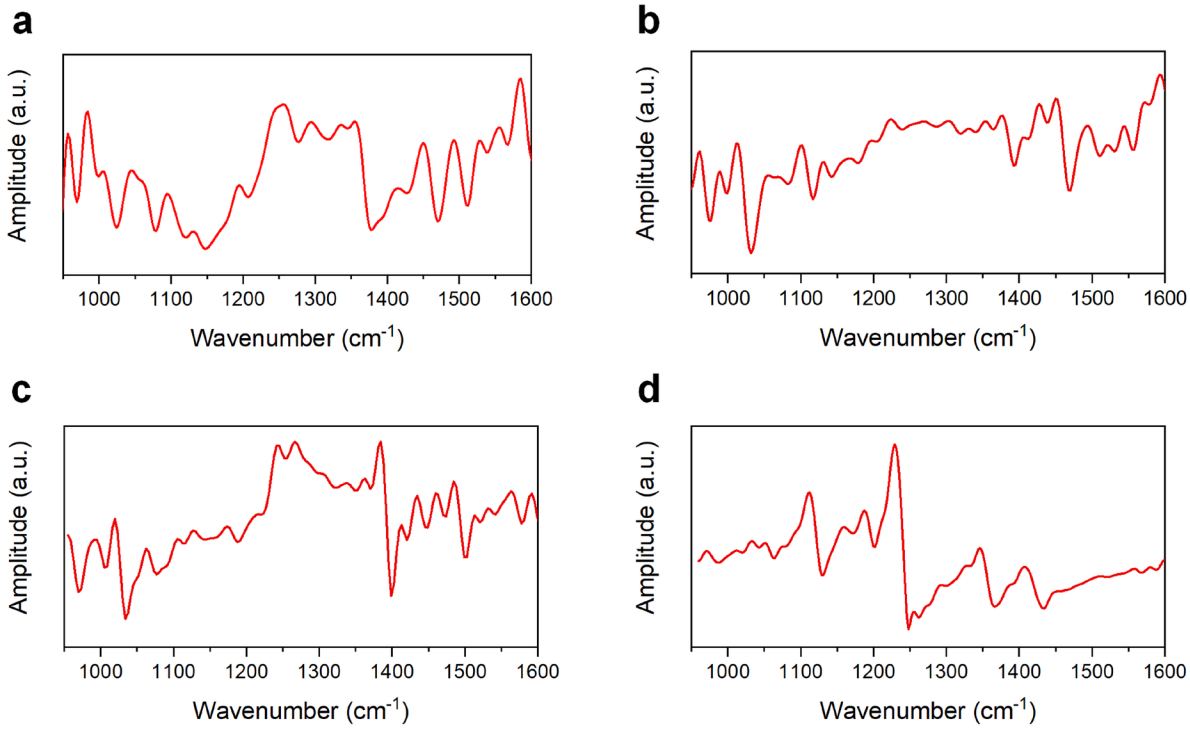

Figure S3. Second demodulation order of the near-field amplitude of (a) TIPS-PEN, (b) TIPS-TAP, (c) Rubrene and (d) PDIF-CN_2 single crystals.

Table of IR modes of TIPS-PEN single crystal

Table S1. Peak positions in cm^{-1} for all the modes observed for a TIPS-PEN crystal at different polarizations with the three techniques. DFT positions (in cm^{-1}) that were calculated for a single molecule of TIPS-PEN in the gas phase are also included. The intensity of the peaks is indicated with bold font – strong, regular font – medium, in brackets – weak. 'x' indicates that there exists a peak but is not well-resolved; '-' indicates that the corresponding peak is absent.

TIPS-PEN	FT-IR	AFM-IR	IR-SNOM	DFT
0°	991 1008/1015 (1063)/(1076) 1139 1176 - (1366)/1379 **1461** (1478) 1528 (1548)	(992) x/x x/x (1138) 1176 1262 **1370**/1376 **1460** x **1530** 1546	**992** **1014** 1069 1137 - 1267 **1367** **1460** - (1525) -	908 933 1035 1111 (1147) 1295 (1341) **1422** (1430) 1516 (1550)
45°	992 1008/(1014) (1061)/1075 (1138) - - 1366 **1463** - (1528) -	(994) x/x x/x (1138) - 1262 **1370-** **1460** x - -		
90°	992 1008/1015 (1061)/1075 (1138) (1176) - 1366 **1463** - (1528) (1547)	(992) x-x x-x (1138) (1176) 1262 1370/(1380) **1460** x 1530 (1546)		

135°	991 1015 (1061)/1077) 1138 1176 - 1379 **1461** (1478) 1528 (1548)	(992) x/x x/x (1138) (1176) 1262 **1370**/1380 **1460** x 1530 (1546)

Table of IR modes of TIPS-TAP single crystal

Table S2. Peak positions in cm^{-1} of all modes observed for a TIPS-TAP crystal at different polarizations with the three techniques. DFT positions (in cm^{-1}) that were calculated for a single molecule of TIPS-TAP in the gas phase are also included. The intensity of the peaks is indicated with bold font – strong, regular font – medium, in brackets – weak. 'x' indicates that there exists a peak but is not well-resolved; '-' indicates that the corresponding peak is absent.

TIPS-TAP	FT-IR	AFM-IR	IR-SNOM	DFT
0°	(994) (1017)/**1032** (1067) **1114** (1136) 1179 - **1315** (1384) **1432** **1460** **1527**	(994) 1022/x (1068) 1114 1134 1178 1228 **1314** **1384** **1432** **1460** **1526**	992 **1022**/- (1052)/(1079) 1112 1134 1179 1227 1310 **1385** 1432 **1462** 1525	910 1031/**1053** 1074 1108 1117 1172 (1288) 1360 1417 1434 **1438** **1522**
45°	(994) (1023)/(1032) - (1114) (1136) - - - (1386) (1432) **1464** (1527)	(990) 1020/x - - (1134) - 1228 - **1384** - **1460** (1526)		

90°	(994) (1022)/1032 - 1114 - (1179) - (1315) (1385) 1432 **1464** 1527	(992) 1020/x - - (1136) (1178) (1228) **1314** **1384** (1432) **1460** 1526
135°	(994) (1016)/**1032** (1067) **1114** - 1179 - **1315** (1383) **1432** **1461** **1527**	(994) 1016/x (1068) (1114) 1134 1178 1228 **1314** **1382** **1432** **1460** **1530**

Table of IR modes of rubrene single crystal

Table S3. Peak positions in cm^{-1} for all the modes observed for a rubrene crystal at different polarizations with the three techniques. DFT positions (in cm^{-1}) that were calculated for a single molecule of rubrene in the gas phase are also included. The intensity of the peaks is indicated with bold font – strong, regular font – medium, in brackets – weak. 'x' indicates that there exists a peak but is not well-resolved; '-' indicates that the corresponding peak is absent.

rubrene	FT-IR	AFM-IR	IR-SNOM	DFT
0°	(967) 1031 (1069) - - - (1216) 1309 (1393) - **1440** **1465** (1494) -	(968) **1028** (1070) (1110) - - (1216) (1308) **1394** - **1440** **1464** - (1572)	962 **1027** 1070 (1109) - - - - **1392** 1417 1442 1467 **1492** 1571	(982) **1053** 1105 (1157) (1198) (1212) (1249) (1338) 1397 **1424** 1481 1512 **1537** (1580)
45°	968 1031 (1069) - (1149) (1171) (1216) 1309 (1393) (1413) **1441** **1465** (1494) (1574)	**968** **1028** 1068 (1110) (1148) (1170) - (1308) **1394** (1412) **1440** **1464** **-** 1574		

90°	968 1030 1068 - 1149 1171 - (1308) (1393) (1413) **1441** **1465** - 1575	**968** **1028** 1068 (1110) (1148) (1170) - (1308) **1394** (1412) **1440** **1464** - 1574
135°	968 1031 1069 - (1149) (1170) (1216) 1309 (1393) (1413) **1441** **1465** (1494) (1574)	968 **1028** (1068) (1110) (1148) (1170) - (1308) **1394** (1412) **1440** **1464** - (1572)

Table of IR modes of PDIF-CN_2 single crystal

Table S4. Peak positions in cm^{-1} for all the modes observed for PDIF-CN_2 crystal at different polarizations with the three techniques. DFT positions (in cm^{-1}) that were calculated for a single molecule of PDIF-CN_2 in the gas phase are also included. The intensity of the peaks is indicated with bold font – strong, regular font – medium, in brackets – weak. 'x' indicates that there exists a peak but is not well-resolved; '-' indicates that the corresponding peak is absent.

PDIF-CN_2	FT-IR	AFM-IR	IR-SNOM	DFT
0°	(1059) **1114/**(1124) - **1221**/1247 (1352)/1362 (1411)/(1427)	**1040/1056** **1114/1124** **1194** **1248** **1350/1360** **1412/1426**	(1039)/(1056) 1123 1196 **1244** 1356 1421	(1056)/**1068** **1119/1128** (1183) **1214/1220** **1339/1354** (1419)/**1437**
45°	(1059) **1114**/ (1124) - 1221/1247 1352/1362 (1411)/(1427)	1040/1058 1114/1122 (1194) 1248 1352/1360 1410/1426		
90°	(1059) 1124 - (1221)/**1247** **1351** (1413)/(1427)	**1040/1056** **1112/1124** **1194** **1246** 1350/1358 1412/1426		
135°	(1058) **1114**/1124 - **1221/1247** 1351/1362 1413/1427	1042/1056 **1112/1124** (1194) **1248** 1350/1360 1412/1426		

FT-IR absorbance spectrum of spin-coated PDIF-CN_2 film

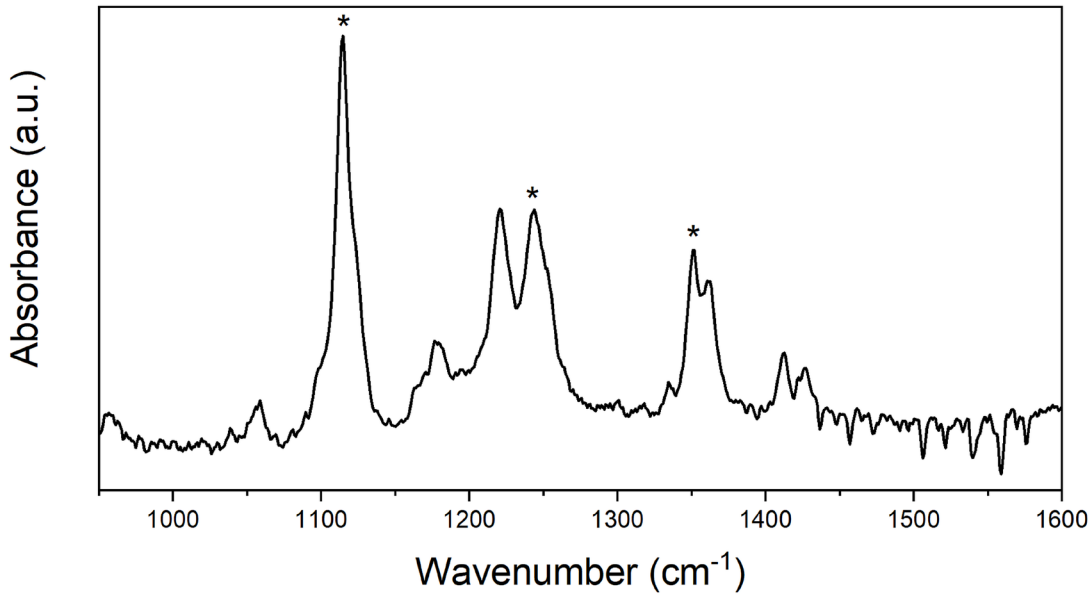

Figure S4. FT-IR absorbance spectrum of a spin-coated, polycrystalline film of PDIF-CN_2. Asterisks indicate those peaks which showed a noticeable difference in the AFM-IR and IR-SNOM spectra from the center and the edge.

Single Spot AFM-IR spectra of PDIF-CN_2 crystallites

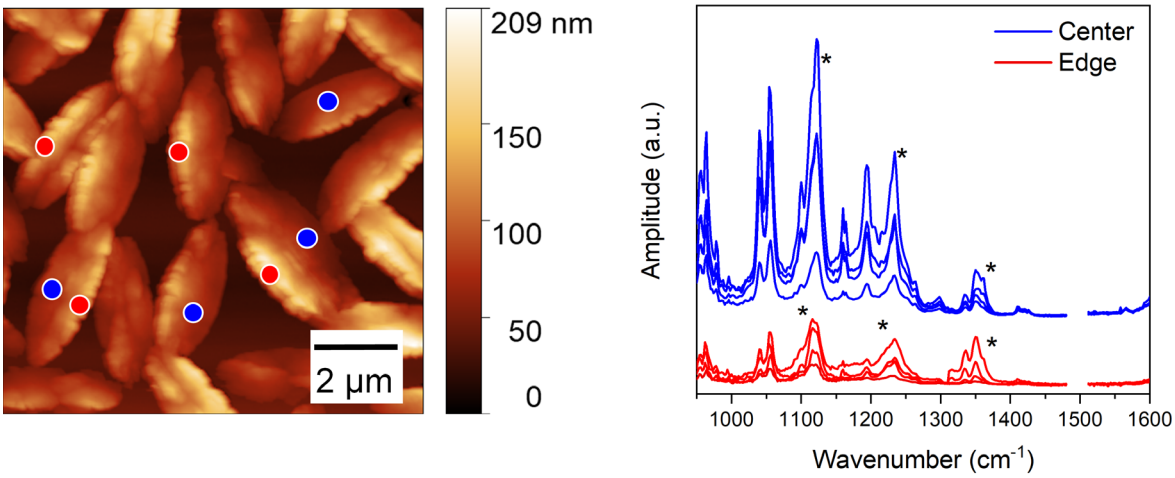

Figure S5. Topography image of spin-coated PDIF-CN_2 film with blue (center) and red (edge) dots indicating the spots where full AFM-IR spectra (blue and red lines, respectively) were recorded.

Overlay of topography and amplitude images from AFM-IR

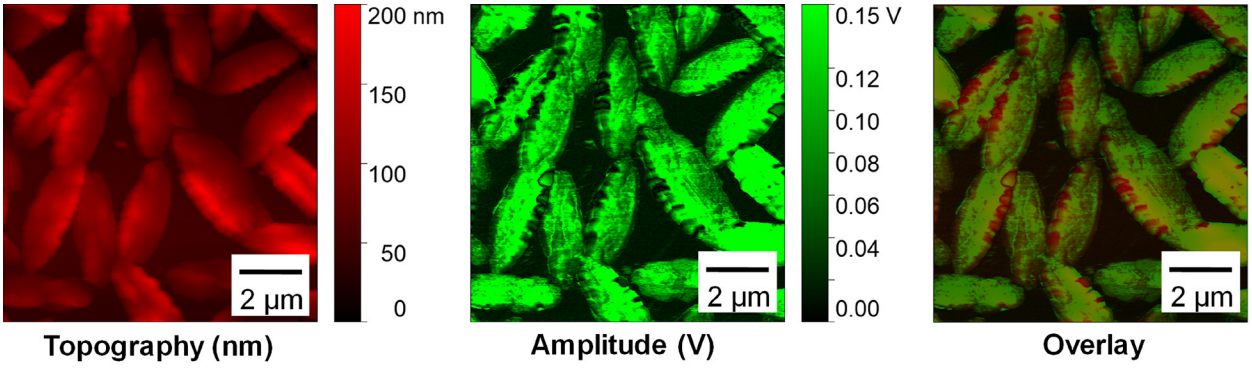

Figure S6. Topography (red) and amplitude (green) images of spin-coated PDIF-CN_2 film mapped at 1234 cm^{-1} with the AFM-IR, and the corresponding overlay. The overlay image shows that there is material at the edges of the crystallites where the amplitude image shows little to no signal.

Single Spot IR-SNOM spectra of PDIF-CN_2 crystallites

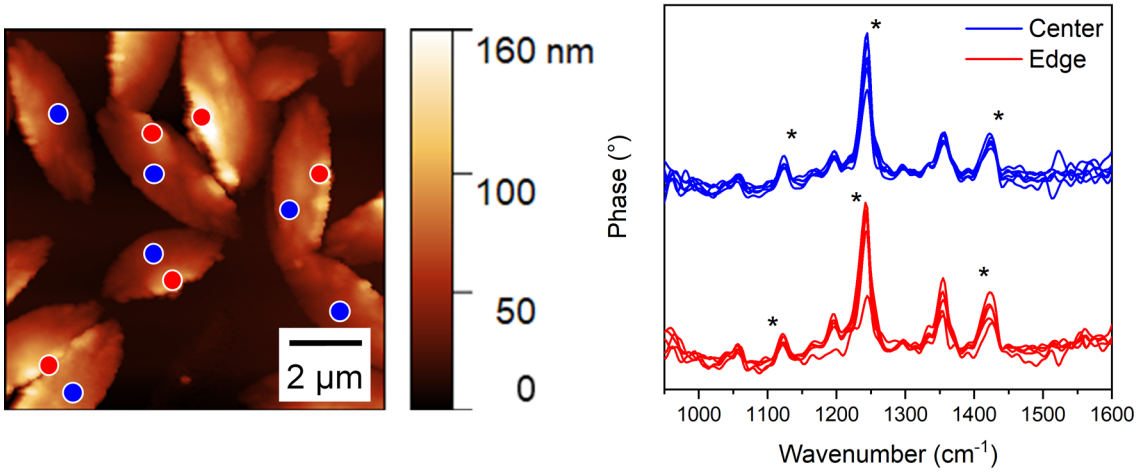

Figure S7. Topography image of spin-coated PDIF-CN_2 film with blue (center) and red (edge) dots indicating the spots where full IR-SNOM spectra (blue and red lines, respectively) were recorded.

IR-SNOM imaging of PDIF-CN_2 film at 1084 cm^{-1}

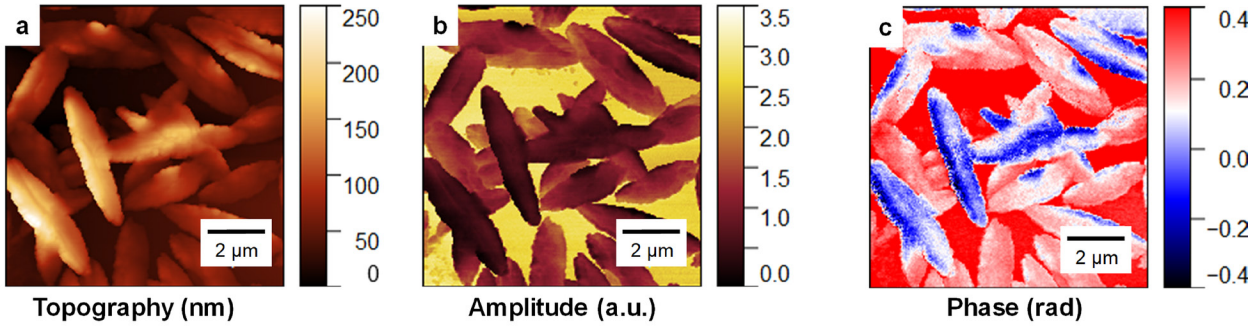

Figure S8. Topography (a), near-field amplitude (b) and near-field phase (c) images of spin-coated PDIF-CN_2 film mapped at 1084 cm^{-1}.